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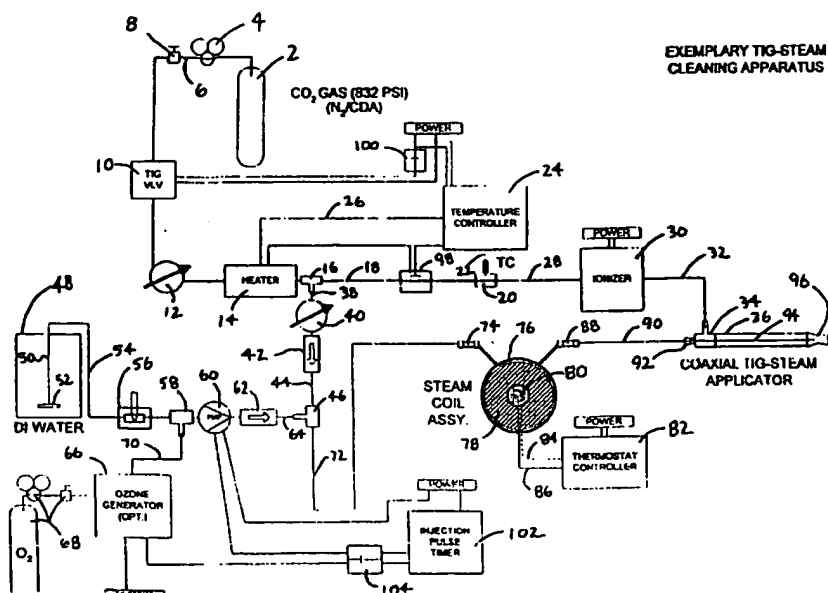
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**(54) Title: GAS-VAPOR CLEANING METHOD AND SYSTEM THEREFOR**



(57) **Abstract:** Disclosed is a method and apparatus for cleaning using a gas-vapor mixture. A heated, pressurized stream of propellant gas is supplied to the outer tube of a coaxial delivery line. The coaxial delivery line is formed of an outer tube and an inner tube operably connected to a divergent-convergent mixing nozzle. A stream of a pre-heated gas is mixed with deionized water to form a gas-liquid mixture, which is heated to form a gas-vapor mixture. The gas-vapor mixture is then fed to the inner tube of the coaxial delivery line. The gas-vapor mixture spray exiting the mixing nozzle is then directed at an article to be cleaned.



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*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## **GAS-VAPOR CLEANING METHOD AND SYSTEM THEREFOR**

### **BACKGROUND OF THE INVENTION**

#### **1. Field of the Invention**

The present invention relates to the chemical arts. More particularly, the invention relates to a system for cleaning using gas-vapor mixtures.

#### **2. Discussion of the Related Art**

High pressure steam and solvent spray cleaning systems are often employed for cleaning various types of mechanical, electrical and fluid components and other articles. Unfortunately, traditional high pressure solvent cleaning systems use very large quantities of solvents, the disposal of which creates an environmental problem, especially with the use of organic solvents such as 1,1,1 trichloroethane and alcohol. Efforts have been made to overcome this problem by making suitable alternative cleaning systems that require much less solvent and thereby substantially reduce the solvent waste problem, for example steam cleaning and supersonic liquid spray devices. Unfortunately, most low flow rate systems cannot provide adequate cleaning of the components. In addition, conventional steam cleaning systems produce very wet substrates, do not allow for spray pressure and temperature control and are typically very bulky - making them difficult to use for cleaning small precision electronic and mechanical devices. Moreover, conventional supersonic liquid spray systems can produce electrostatic charges during post drying operations which can damage sensitive electronic devices being cleaned.

Examples of conventional steam spray devices include the micro precision steam cleaner from Va-Tran Systems, Chula Vista, Ca. The device uses a supply of deionized water which is pumped into a heating coil and the resulting steam spray is jetted at a substrate using a hose and handheld spray wand. The system is actuated using a solenoid footswitch. Another commercial cleaning device is the Gem Steamer, available from Shor International Corporation, Vernon, N.Y. The Shor device is similar to the Va-Tran device except it has a fixed spray head attached to the steamer unit and a substrate to be cleaned is positioned in front of the fixed steam spray head. This unit features a footpedal actuator as well. It is a drawback of these conventional systems that they do not provide a capability for dynamically changing the spray pressure (velocity) or temperature during cleaning, or for in situ drying or for electrostatic control.

Another drawback of the conventional systems is that residual condensed steam typically remains within a conventional steam heating coil during an extended steam cycle,

which cools down the heating coil and condenses the steam into hot water. This condensed phase tends to spit or sputter from the steaming unit following de-actuation - flooding the substrate with a pool of residual hot water. This characteristic is a typical by-product of conventional steam cleaning because a relatively large quantity of water is needed to produce an adequate mixture of steam/vapor for providing both cleaning velocity (mechanical energy) and cleaning solvency (chemical/thermal energy). Yet another drawback of conventional steam cleaning systems is that they have designs and operational characteristics that greatly limit the ability to automate the cleaning process - as these systems tend to be manually operated.

Another commercialized alternative cleaning system employs small amounts of liquids with propellant-based velocity control and is disclosed in U.S. Patent No. 5,730,806 to Caimi et al. This patent discloses a high velocity gas-liquid spray wherein a small quantity of liquid (i.e., water or organic solvent) is accelerated to substantially sonic velocity using a high pressure gas to create shear stress at the surface of a substrate to be cleaned. This device also suffers from a number of drawbacks. For example, the device employs a liquid-phase cleaning agent below its boiling point which requires drying the substrate following spray cleaning operations. In addition, a danger exists that following spray cleaning, electrostatic charges may be generated during drying that, if not eliminated, may damage static sensitive substrates. Moreover, the liquid phase cleaning agent must be accelerated at very high velocity in order to produce adequate shear. It is also a drawback of both the steam spray cleaning devices and the gas-liquid supersonic cleaning devices that they require a secondary drying gas jet such as heated air or infrared heat to mitigate condensation and remove residual liquid phase residues from the substrate, or from between a substrate interface.

U.S. Patent No. 5,725,154 to Jackson teaches a spray gun for cleaning that uses solid CO<sub>2</sub> (dry ice) in combination with a heated inert and ionized propellant gas. The patent teaches the use of a coaxial delivery tube having an outer tube and an inner tube operatively attached to a divergent-converged mix nozzle. The propellant gas flows through the outer tube while the solid CO<sub>2</sub> flows through the inner tube. Such a dry ice cleaning method cannot be used in applications where thermal energy or wet oxidation chemistry are necessary for proper surface cleaning. However, tenacious contaminants such as waxy or resinous compounds require such high temperatures or wet oxidation chemistry before they can be removed.

From the above, it is seen that there is a definite need for a method and apparatus for cleaning articles that offer enhanced cleaning and drying capability and is safe, easy, and reliable and can be easily integrated with automation and control systems. The present invention satisfies these and other related needs and provides further related advantages.

### **SUMMARY OF THE INVENTION**

The present invention overcomes the deficiencies of prior art cleaning systems. The present invention employs variable velocity, variable thermal energy, inter-transport phase change and interphasic contaminant-substrate separation mechanisms instead of using relatively high propellant pressures and/or relatively large quantities of heated or unheated cleaning agents to perform the same cleaning task.

The invention provides, *inter alia*.

- 1) for the use of minimal amounts of deionized water;
- 2) for significantly lower pressures than are employed in conventional high pressure steam and solvent cleaning systems;
- 3) for a continuous source of heat energy and ions within a propellant stream to provide controlled condensation and mitigation of electrostatic charges during delivery, cleaning, and drying;
- 4) for carbonated steam to enhance particle entrainment and separation; and
- 5) for continuously preheating, carbonating, and ozonating the deionized water and discharging condensed steam residues from an inner capillary heating coil, following steam generation so as to prevent sputtering of substrate with residual steam condensates formed within the heating coil and inner coaxial delivery line.

In accordance with the inventive method, a heated, pressurized stream of propellant gas, preferably of carbon dioxide, is supplied to the outer tube of a coaxial delivery line. The coaxial delivery line is formed of an outer tube and an inner tube operably connected to a divergent-convergent mixing nozzle. A stream of a pre-heated gas is mixed with deionized water to form a gas-liquid water mixture, which is heated to form a gas-water vapor mixture. The gas-vapor mixture is then fed to the inner tube of the coaxial delivery line, the gas-vapor mixture spray exiting the mixing nozzle, at supersonic rates in some embodiments, is directed at an article to be cleaned to clean the article using the resulting gas-vapor mixture spray.

In some embodiments, the propellant gas has a temperature of 150° F. to 350° F. when it enters the coaxial delivery tube and, in some embodiments, the propellant gas has a pressure between 60 and 300 psi when it enters the coaxial delivery tube. In some embodiments, the deionized water is ozonated and, in some embodiments, the propellant stream is ionized. And in some embodiments, the gas-liquid mixture is heated with a capillary steam generation system.

An inventive apparatus useful in accordance with the method includes a source for the heated, pressurized propellant gas stream and a coaxial delivery line formed of an outer tube and an inner tube operatively connected to a nozzle, with the outer tube in fluid communication with the propellant gas stream source. In preferred embodiments, the coaxial delivery tube is made of stainless steel, Teflon, polyetheretherketone or combinations thereof.

The apparatus also includes a mixer for mixing deionized water with the pre-heated gas stream. The apparatus employs a capillary steam generation system for receiving the gas-liquid mixture and forming a gas-vapor mixture from the gas-liquid mixture.

In some embodiments, the apparatus additionally includes an ionizer for ionizing the propellant gas, located between the gas propellant source and the outer tube and in some embodiments, the apparatus additionally includes an ozone generator to ozonate the deionized water.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

The features and advantages of the present invention will become apparent from the following detailed description of a preferred embodiment thereof, taken in conjunction with the accompanying drawings in which:

Fig. 1 is a schematic diagram of a gas-vapor cleaning system in accordance with the present invention.

Fig.'s 2A and B are plan views of the front and rear panels of a device in accordance with the invention along with certain related components.

Fig. 3 is a cutaway side view of a divergent-convergent mixing nozzle.

Fig. 4 is an end view of the divergent-convergent mixing nozzle shown in FIG. 3.

Fig. 5A is a diagram illustrating the relationship between velocity and viscosity and contact time.

Fig. 5B is a diagram illustrating the relationship between cleaning energy and contact time.

Fig. 5C is a flow diagram illustrating one embodiment of the process in accordance with the invention.

Fig. 6 is a diagram illustrating the dynamics of the process shown in Fig 5C.

Fig. 7 is a block diagram illustrating gas-vapor cleaning incorporated into a process that includes attaching a die to a substrate.

### **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

Following is a more detailed consideration of the preferred embodiments of the present invention. FIG. 1 illustrates a gas-vapor cleaning system in which a pressurized and regulated propellant gas is supplied from a gas supply tank 2. Any suitable inert gas can be employed as the propellant gas. Suitable propellant gases include, argon, steam, nitrogen, clean, dry air, and carbon dioxide, with carbon dioxide being most preferred. The propellant gas flows from the supply gas tank through an inlet gas pressure regulator 4, an inlet gas line 6 and an inlet gas supply shutoff valve 8 to an inlet of a pneumatic or electrical solenoid valve 10. From the solenoid valve 10, the propellant gas flows through interconnecting gas pressure regulator 12, which can vary the propellant gas pressure from between 20 and 3000 psi, preferably between 60 and 300 psi, and into an in-line electrical resistance heater 14 which heats the propellant gas from ambient temperature to a temperature from between 150° F, and 350° F. The heated gas exits the heater 14 and flows into a tee connection 16 wherein the heated gas is fractionated into two streams; a pre-heated gas stream and a propellant gas stream.

The propellant gas stream flows through an interconnection line 18 and through a tee 20 containing a thermocouple 22. The thermocouple 22 is connected to the thermocouple input of a temperature controller 24. The temperature controller 24 outputs power through power connection 26 and turns on and off the heater 14 based on the temperature controller's adjustable temperature control dial (not shown) and as set by the user, and the thermocouple 22 measurement. The preferred temperature range for the propellant gas is between 150° F and 350° F. A number of commercial suppliers of thermocouple devices and temperature controllers are available and suitable for use in the present invention.

The heated propellant gas stream flows from the thermocouple tee 22 through an interconnection line 28 and through an in-line ionizer 30, available from Ion Systems, Berkeley, CA, wherein the propellant gas is ionized to provide both positive and negative ions within the propellant gas stream. The heated propellant gas stream flows from the ionizer 30 through interconnection line 32 and into a coaxial tee 34, wherein the propellant



gas is fed into a flexible or rigid outer tube 36. The propellant gas then flows over the inner tube 94, bathing said inner steam tube in heated gas, and then the propellant gas is mixed in a divergent-convergent mixing nozzle 96. Preferably the outer tube is constructed of stainless steel, and/or Teflon and/or polyetheretherketone (PEEK).

Returning to the inlet gas stream split tee 16, the pre-heated gas stream flows through an interconnection line 38, through an in-line pressure flow regulator/reducer 40, through an in-line check-valve 42, and through an interconnection line 44 into a fluid mixing tee 46. At this point the gas stream is mixed with deionized water and, in some embodiments ozonated, as follows.

Deionized water, preferably having a resistivity of at least 18 Mohms, contained in a suitable reservoir bottle 48 and containing a syphon tube 50 and suction particle filter 52, is delivered via an interconnection line 54 through a micrometering flow control valve 56, through an ozonation tee 58, into an oscillating piston micropump 60 (available from E. Clark Associates, Clinton, MA), in-line check-valve 62 and into fluid mixing tee 46 via interconnection line 64. It is a distinct advantage of the invention that only small quantities of deionized water, on the order of only 1 to 100 mls/min., are required. The ozonation system comprises a commercial ozonator 66 (available from Ozonia Inc., Elmwood Park, NJ) which is connected to a supply of ultra-dry pressure-regulated oxygen gas 68 or clean dry air. The ozonated feed gas created by said ozonator 66 flows into the ozonation tee 58, under its own pressure, via an interconnection line 70 and mixed with the deionized water in ozonation tee 58 prior to being pumped by the micropump 60 into the fluid mixing tee 46.

Returning to the fluid mixing tee 46, the gas stream is mixed with the deionized water stream, whereupon the deionized water stream is preheated and carbonated, in those embodiments where carbon dioxide gas is used as the gas, under pressure. The preheated, carbonated, and ozonated deionized water is fed via interconnection line 72 into the inlet 74 of a capillary tube coil 76, whereupon the mixture is heated from gas-liquid state to gas-vapor state as follows.

The capillary steam generation system comprises a solid metal cylindrical block 78 containing circumferential grooves (not shown) wherein a capillary tube coil, preferably made of stainless steel, is wrapped around a heated cylinder block 78, preferably made of copper, and embedded in said circumferential grooves to provide intimate contact with the heated cylinder block 78. The diameter, loop length, and insertion heater capacity are chosen to provide the gas-vapor production capacity and temperature required for a particular application. A variety of capillary tube diameters, loop lengths, and insertion

heater capacities can be used to provide the proper gas-vapor production capacity and temperature required for different applications. An insertion heater 80, which has a built-in thermocouple device, runs through the interior of cylinder block 78 and is in intimate contact with the central mating surfaces. The insertion heater 80 is connected to a thermostat control device 82 which measures the internal thermocouple measurement signal 84 from the insertion heater 80 and provides electrical power 86 to the insertion heater based on the control setting input on the thermostat device 82. The steam generation temperature range is between 212° F to 500° F, preferably between 250° F and 350° F.

The vaporized-water mixture 88 exits the capillary tube coil 76 and is fed via an interconnection line 90 to a bulkhead tube-tube connector 92, wherein it is integrated with a coaxial tee 34.

The various interconnection lines, tubes, fittings, tees, and other components are constructed of stainless steel, Teflon PEEK or combinations thereof. Wetted surfaces of solenoid valves, regulators and check valves are constructed of stainless steel, Teflon or PEEK. These components should be rated for the high operating temperatures and moderate pressures employed in accordance with the present invention.

A rigid or flexible inner tube 94, constructed of stainless steel, PEEK or combinations thereof, is connected to a bulkhead tube-tube connector 92 and is centered within the outer tube 36. This provides a coaxial delivery line 136. The line can be of various lengths and diameters. The maximum length of the coaxial delivery line is determined by the ability to maintain vapor conditions within the coaxial delivery line to the point of discharge. The coaxial delivery line 136 is connected to a stainless steel, Teflon or PEEK propellant gas-steam divergent-convergent mixing nozzle 96.

The various fluid flow control, heating, pumping, ionization and ozonation devices are powered and controlled by any suitable means. In one embodiment, devices requiring power and control are divided into two control circuits. The system for controlling the propellant gas is formed of one of the control circuit and includes the solenoid valve 10, temperature controller 24 and inlet gas heater 14, and, in some embodiments, the heated propellant ionizer 30. The system for controlling the steam generation is formed of the other control circuit and includes the deionized water injection micropump 60 and, in some embodiments, the ozonation device 66. Both are controlled using an injection pulse cycle timer 102.

The propellant gas heating system can be manually or automatically controlled. It includes the in-line gas heater 14, the temperature controller 24, and the thermocouple 22,

along with a propellant gas pressure switch 98. The pressure switch 98 ensures that the heater is not powered in the absence of gas flow through the solenoid valve 10. Power in the form of 110 to 240 VAC is provided to the temperature controller 24 and ionizer 30 directly upon power-up using a main control switch (not shown). The solenoid valve 10 is powered through a propellant gas relay switch 100 connected to a conventional footpedal control (not shown) or using an electromechanical relay controlled by a PLC/PC with appropriate software. When actuated, the propellant gas relay switch 100 provides power to the solenoid valve 10. The pressure switch 98 detects the pressure and an internal relay contact closes, providing power to the heater, received through the temperature controller 24. The temperature controller 24 cycles power to the heater 14 through the pressure switch 98, based upon the match between the thermocouple 22 input and the temperature controller 24 setting. The ionizer 30 having already been actuated ionizes the heated propellant as it passes through the ionizer.

The steam generation system can be manually or automatically controlled. It includes the deionized water injection micropump 60 connected to a pulse cycle timer 102, to regulate the injection periods for the deionized water into the steam generator circuit. The pulse cycle timer 102 is connected to a steam injection relay 104 which can be connected to a common footpedal control (not shown) or, using an electromechanical relay, controlled by a PLC/PC with appropriate control software. When actuated, the steam injection relay switch 104 provides power to the micropump 60 which, in combination with the pulse cycle timer's 102 internal intermittent power control relay, provides a period of on-state and a period of off-state, both being varied between 0.5 seconds and 5.0 minutes, preferably between 0.5 seconds and 5.0 seconds. This circuit meters or controls the amount of the deionized water mixed with the pre-heat gas stream at fluid mixing tee 46, the injection of the water mixture into the steam generation system at coil connection 74 and which is subsequently mixed with the propellant gas at mixing divergent-convergent mixing nozzle 96. In those embodiments including the ozonation device 66, the device is also controlled using the steam injection relay and pulse timing circuit used with the propellant gas heating system, wherein the ozonator is turned on and off to provide ozonated gas at the ozonation mixing tee 58 which is mixed with the deionized water prior to the inlet of the micropump 60. Power is provided to the heating cylinder insertion heater 80, through thermostat controller 82, upon main power start-up. The thermostat controller 82 heats the insertion heater 80 and cylinder 78 to a setting that is dialed on the thermostat

controller 82. Heating to the desired gas-vapor mixture temperature is controlled through applied power and time.

Having thus described the apparatus, along with the operation and control circuits, the following is a discussion of the general operation of the mixing nozzle 96. The deionized water is pulse injected into the capillary tube coil and is heated to its vaporization point and delivered down the coaxial delivery line 136 within the centrally located inner tube 94 which is in indirect contact with heated gas propellant contained within the outer tube 36. The two streams are first conductively-mixed and then contactively-mixed within the divergent-convergent mixing nozzle producing a superheated steam aerosol mixture. The gas-vapor mixture is then ejected as a variable geometry spray mixture, *i.e.*, a mixture whose chemistry, temperature and velocity can be varied. The gas-vapor mixture stream is then ejected from the end of the divergent-convergent mixing nozzle 96 where it is directed by an operator or robot onto components or articles that require cleaning. The energy imparted to the gas-vapor mixture through momentum transfer and nozzle profile (Bernoulli Principle) gives the gas-vapor mixture sufficient cleaning energy during impact, and during subsequent condensation shearing action described herein, to remove contaminants on the surface, or within interfaces, of the component being cleaned.

Fig.'s 2A and 2B illustrate a front and rear control panel and related components for the inventive apparatus, respectively. Referring to Fig. 2A, filtered deionized water 106 is supplied to a liquid inlet orifice 108. The deionized water is pumped into the system at a rate of, for example, 1.0 mls/min to 100 mls/min, preferably between 1.0 and 50 mls/min., and in some embodiments, mixed with ozone at a concentration of 0.5% to 6 0% by volume. The deionized water is then injected into the carbonation tee, and injected into the steaming unit. Filtered carbon dioxide gas 110 flows into the gas inlet orifice, 112 and is internally heated and, in some embodiments, ionized at a pressure and flowrate of, for example, 20 psi to 3000 psi and 5 to 150 scfm, preferably between 60 psi and 300 psi and 10 to 50 scfm. Electrical power to the cleaning system is provided using a power cable 114 and power input connection 116. A communication connection device 118 is interfaced using a cable (not shown) with a PLC/PC control system to provide remote control of the cleaning system using an analog/digital control system and software.

Turning to Fig. 2B, it can be seen that the back panel features an additive inlet connection orifice 119, which allows for connection to an external ozone generator and delivery system (not shown).

As shown in Fig. 2A, the on/off control device for the present invention includes a dual footpedal 120. One footswitch 122 is used to actuate the steam relay switch 104 (Fig. 1) and propellant gas relay switch 100 (Fig. 1) simultaneously to operate pulsed propellant gas-steam cleaning and drying operations. A second footswitch 124 is used to actuate the propellant gas relay 100(Fig. 1) only for ionized gas substrate drying and deionization operations only.

The cleaning system features a main power switch 126 which, when actuated, delivers electrical power to the electronic devices. The front panel features controls for the propellant gas, including the thrust pressure regulator 12 and the digital temperature controller 24. The front panel also features separate controls for steam generation including the digital pulse cycle timer 102, an on/off switch 128 for the micropump 60, which turns off power between the pulse timer 102 and micropump 60, and a micrometering flow control valve 56 which controls the flowrate of deionized water from the reservoir 48 through delivery input line 54 and into the micropump 60. The front panel has a bulkhead connection 130 for the coaxial delivery line 132 comprising the outer tube 36 and containing therein the inner tube 94. The spray applicator comprises a handgun assembly 134 containing the end-most part of the coaxial delivery line 132 and containing the propellant gas steam divergent-convergent mixing nozzle 96. A handgun assembly 134 protects the operator from thermal burns and aids in directing the spray applicator.

In an alternative embodiment, the micropump 60 is substituted with a gas pressurized (*i.e.*, carbon dioxide gas) reservoir bottle containing the deionized water. Using a solenoid valve, connected to the pulse cycle timer 102, the desired quantities of carbonated-ozonated deionized water can be metered into the steam generation system.

A divergent-convergent mixing nozzle useful in accordance with the invention is illustrated in Fig. 3. The nozzle 96 includes an outer nozzle body 135 which contains a gradual and cylindrically convergent surface 136 wherein the propellant is compressed from a larger diameter region 137 to a smaller diameter region 138. At the center of the nozzle body 135 is contained the inner tube 94, wherein steam is delivered into the convergent compression zone 138. The steam as it exits is compressively mixed with the propellant gas resulting in either an increase or decrease in temperature (depending predominantly upon the temperature of the propellant gas due to its higher mass flow) and resulting in either a subsonic or supersonic velocity (depending upon the nozzle configuration and propellant gas mass flow). The propellant gas-steam mixture exits the compression zone 138 and is

accelerated through the divergent expansion zone 140 and out of the end of the spray nozzle section 142.

Fig. 4 shows an end view of the divergent-convergent mixing nozzle 96. There can be seen the inner tube 94, the divergent nozzle zone 140, the convergent mixing zone 138, and the nozzle body 138. Various nozzle designs can be constructed out of various materials such as Teflon, stainless steel, PEEK, and anodized aluminum. The inner convergent-divergent geometry and overall nozzle body design can be manufactured to produce different spray patterns, for example a flat wide spray or a high velocity pin-point spray.

The inventive process can be described, in part, as a kinetic energy transfer process called "Linear Momentum Transfer" in accordance with the following vector quantity:

$P = MV$ , where

$P$  - Linear Momentum of Carbonated Steam Aerosol Particle or Surface Particle

$M$  - Mass of Carbonated Steam Aerosol Particle or Surface Particle

$V$  - Velocity of Carbonated Steam Aerosol Particle or Surface Particle

A stream of condensing and supersonic vapor having increasing significant mass and velocity, as maintained by the presence of propellant gas, impacts a stationary surface particle causing the surface particle with a given mass to accelerate away from the surface to a given velocity in accordance with the following equation:

$V_{sp} = (M_{cp}/M_{sp})V_{cp}$ , where

$V_{sp}$  - Velocity of Surface Particle

$M_{cp}$  - Mass of Aerosol Particle.

$M_{sp}$  - Mass of Surface Particle

$V_{cp}$  - Velocity of Aerosol Particle

The physical and thermal energy transferred during the decontamination process is usually sufficient to overcome strong electrostatic and intermolecular adhesive forces, commonly referred to as Van der Waal's forces, that hold small particles and residues to the surface.

Moreover, the shearing or drag force on particles can be described using the following equation:

$F_d = (C_p V^2 A)/2$ , where

$F_d$  = Drag Force on Particle or Residue

$C$  = Coefficient of Drag

$\mu$  = Viscosity of Aerosol

$V$  = Velocity of Aerosol

Referring to Fig. 5A, it can be seen that during the controlled condensation of the gas-vapor mixture from a gas-vapor interphase to a gas-liquid interphase on the substrate, cleaning agent mixture viscosity is dramatically increasing - thus viscous drag force is increasing dynamically on the surface. Moreover, propellant gas pressure is controlled dynamically as well, increasing (or decreasing) the velocity of the condensing aerosol and further increasing shearing force upon surface residues in accordance with the drag force equation. Thus, as shown in Fig. 5B, the cleaning energy of the system is increasing during the application of the propellant gas-vapor spray mixture.

Another mechanism for the removal of trace organic films using the present invention is a combination of momentum transfer and an interphase change of minute aerosols from gas-vapor to gas-liquid, called "Condensation Shearing", and the subsequent entrainment and solutioning of trace surface residues under a variable shearing force.

A further separation mechanism involves the formation of microscopic cleaning substances called "Carbonated Aerosols". Carbonated aerosols are comprised of small amounts of carbonic acid, carbon dioxide gas (and, in some embodiments, ozone gas) which are dissolved within the condensing phase (liquid state). The presence of dissolved carbon dioxide gas (or ozone gas) within the gas-liquid interphase increases cleaning activity both chemically and mechanically. Carbonic acid increases solvency for various ionic residues by lowering pH and providing active carbonate chemistry, and during application, dissolved carbon dioxide leaving the liquid forms microscopic gas bubbles - producing a scouring action upon the substrate and further enhancing mechanical cleaning action. Still further, the presence of ozone gas within the gas-vapor interphase provides additional oxidative surface cleaning action as well as mechanical scrubbing bubble (foam) cleaning action. The presence of foams on the surface, or between low tolerance interfaces, greatly lowers interfacial free energy (surface tension) - further enhancing particle removal and drying action.

Referring to Fig. 5C, it can be seen that the overall cleaning involves combining a condensable and chemically-enhanced high temperature cleaning agent (*i.e.*, carbonated/ozonated steam) with a variable temperature and non-condensable ionized cleaning agent/propellant gas (*i.e.*, carbon dioxide gas) 144. The propellant gas-steam mixture is directed against a substrate 146 which comprises a Ball Grid Array (BGA) electronic package which has been soldered to a second substrate 148 using solder ball

joints 150. Residual solder fluxing and particulate residues contained between the first and second substrates must be removed prior to underfilling with a non-conductive adhesive. This application of the inventive cleaning process involves rapidly moving the gas-vapor mixture into and through the interfacial region as a supersonic gas-vapor front 152, whereupon the gas-vapor front in contact with the interfacial components (*i.e.*, solder balls) begins to condense 154, wetting, solubilizing and entraining the contaminants. The propellant gas acting as a mechanical cleaning agent, continues to heat and move the condensing front completely through the interfacial region, sweeping the contaminants entrained or solubilized in the mixture from the opposite side 156.

Fig. 6 illustrates the combination of thermal and physicochemical cleaning phenomenon operating in concert during the use of the gas-vapormixture. It can be seen that the gas-vapor interphase front 158 provides immediate heating and penetration of the surface, interfacial regions, and contaminants, the subsequent gas-liquid interphase 160 provides solubilization, oxidation (when ozone gas is present), entrainment and enhanced transport of contaminants. When the pulsing feature is used with the steam injections, the intermittent periods (no injection) remove the residual gas-liquid interphase leaving the interfacial region dry and deionized 162. As shown, during rapid intermittent gas-vapor spray and gas spray only operations, typically separated by a time of between 0.5 and 3 seconds, the entire condensation shear cleaning process can be repeated 164 multiple times. As applied to the substrate cleaning application described above in Fig's. 5A-C, the resulting cleaning action through the substrate interfacial region is a combination of vortexing and multiphasic cleaning and drying actions 166 which continue along a straight path through the entire interface. In the application, the spray applicator may be directed at any angle and from any side of the component as shown by the arrows 168, 170, 172, 174 to provide thorough cleaning and drying of the substrate.

In some embodiments, the inventive process is used to prepare a substrate for subsequent production and assembly operations, such as surface cleanliness inspection, electroplating, chemical vapor deposition, soldering, bonding, adhesive dispensing and the like. In other embodiments, it is used to design application tools which incorporate and integrate one or more production operations which include the present cleaning process into a single process tool.

In some embodiment, the present invention is integrated with a surface inspection technique to verify the cleaning efficacy. One such inspection technique is a non-contact technique that employs optically-stimulated electron emission (OSEE) spectroscopy. OSEE



applies UV radiation to a surface, which then causes the surface to eject electrons. Dirty surfaces absorb UV light and eject fewer electrons than clean surfaces.

In other embodiments, a cleaning device in accordance with the present invention is integrated with an adjunct production process, such as, plasma surface modification, adhesive dispensing, and bonding and soldering machines. Fig. 7 illustrates the integration of the present invention with both surface cleanliness analysis and adhesive dispensing in a single production tool. The integrated cleaning-production tool includes a gas-vapor cleaning applicator 176 with a coaxial delivery line 178 partially shown. Included with the integrated tool is an optically-stimulated electron emission (OSEE) surface analyzer 180, an interfacing cable 182, an adhesive dispensing applicator 184, and adhesive delivery line 186. The integrated tool assembly is connected by a common manifold 188 and robotic attachment 190. A robot or some other automation component (not shown) connects to the robotic attachment 190 and provides movement of the integrated tool in any direction as indicated by multidirectional arrow 192.

The integrated tool illustrates a substrate 194, such as an electronic board, which must have a certain portion of its substrate surface 196 cleaned prior to inspection, adhesive dispensing and placement of a component 198, a die, to the clean and dry surface. Using the integrated tool, the substrate surface portion 196 is: 1) cleaned and dried using the propellant gas-steam applicator 176, 2) inspected for residual residues using the OSEE surface inspection device 180, 3) treated with an epoxy adhesive, whereupon, 4) an electronic die 198 is placed over the substrate portion, 5) the die 200 is attached to the substrate, and 6) the attached die 202 is thermally cured.

The entire cleaning process may be performed within a workcell which is automated and controlled using system software in combination with a PC or PLC, various electronic switches, digital controlled pressure and temperature controllers, and a robot. The integrated system software can be written in Visual Basic operating on a Windows NT and using an Allen Bradley PLC controller. The software embodiment can be used to perform real-time correlation between the OSEE photoemission analysis and the cleaning performance with automatic pressure and temperature adjustments as necessary to achieve the desired surface quality. Operational software may further be used to manage and operate the various system operational and control features described herein.

Although the invention has been disclosed in terms of a preferred embodiment, it will be understood that numerous variations and modifications could be made thereto without departing from the scope of the invention as set forth herein.

**CLAIMS**

1. A method for cleaning an article using a gas-vapor mixture comprising the steps of:
  - supplying a heated, pressurized stream of propellant gas to the outer tube of a coaxial delivery line having an outer tube and an inner tube operably connected to a divergent-convergent mixing nozzle;
  - mixing a stream of a pre-heated gas with deionized water to form a gas-liquid mixture;
  - heating the gas-liquid mixture to form a gas-vapor mixture;
  - supplying the gas-vapor mixture to the inner tube of the coaxial delivery line; and
  - directing the gas-vapor spray exiting the mixing nozzle at an article to be cleaned to clean the article using the resulting gas-vapor spray.
2. The method in accordance with claim 1 wherein propellant gas and the pre-heated gas are carbon dioxide.
3. The method in accordance with claim 1 wherein the propellant gas has a temperature of 150° F. to 350° F. when it enters the coaxial delivery tube.
4. The method in accordance with claim 1 wherein the propellant gas has a pressure between 60 and 300 psi when it enters the coaxial delivery tube.
5. The method in accordance with claim 1 further comprising ozonating the deionized water.
6. The method in accordance with claim 1 further comprising ionizing the propellant stream.
7. The method in accordance with claim 1 wherein the deionized water has a resistivity of at least 18 Mohms.
8. The method in accordance with claim 1 wherein the gas-liquid mixture is heated with a capillary steam generation system.

9. The method in accordance with claim 1 wherein the gas-vapor mixture exits the nozzle at a supersonic rate.

10. A method for cleaning an article using a gas-vapor mixture comprising the steps of:

supplying a heated, pressurized stream of ionized carbon dioxide gas to the outer tube of a coaxial delivery line having an outer tube and an inner tube operably connected to a divergent-convergent mixing nozzle;

mixing a stream of pre-heated carbon dioxide gas with ozonated deionized water to form a carbon dioxide gas-liquid mixture;

heating the carbon dioxide-liquid mixture with a capillary steam generation system to form a gas-vapor mixture;

supplying the carbon dioxide gas-vapor mixture to the inner tube of the coaxial delivery line; and

directing the gas-vapor mixture spray exiting the mixing nozzle at an article to be cleaned to clean the article using the resulting gas-vapor mixture spray.

11. The method in accordance with claim 10 wherein the carbon dioxide entering the coaxial delivery tube has a temperature of 150° F. to 350° F. and a pressure of 60 and 300 psi.

12. The method in accordance with claim 10 wherein the gas-vapor mixture spray exits the nozzle at a supersonic rate.

13. A gas-vapor cleaning system comprising:

a source for a heated, pressurized propellant gas stream;

a coaxial delivery line formed of an outer tube and an inner tube operably connected to a divergent-convergent mixing nozzle, the outer tube in fluid communication with the propellant gas stream;

a mixer for mixing a gas stream with deionized water to form a gas deionized liquid water mixture;

a capillary steam generation system for receiving the gas deionized liquid water mixture and forming a gas-water vapor mixture, one end of the inner tube in fluid communication with the capillary steam generator.

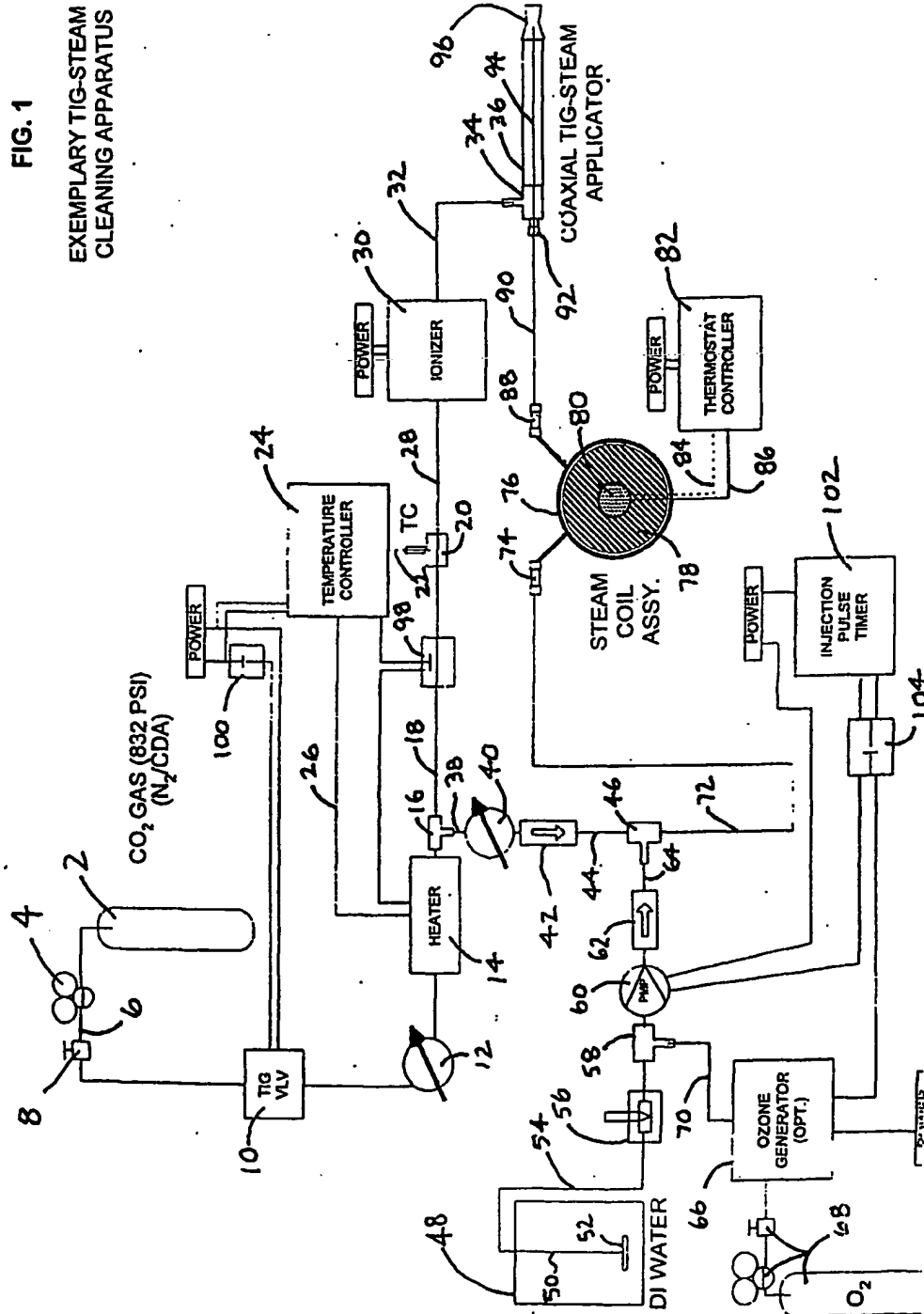
14. The system in accordance with claim 12 further comprising an ionizer for ionizing the propellant gas, the ionizer located between the gas propellant source and the outer tube.

15. The system in accordance with claim 12 wherein the coaxial delivery line is constructed of stainless steel, Teflon, polyetheretherketone or combinations thereof.

16. The system in accordance with claim 12 further comprising an ozone generator to ozonate the deionized water.

17. A gas-vapor cleaning system comprising:  
a source for a heated, pressurized propellant gas stream;  
a coaxial delivery line formed of an outer tube and an inner tube operably connected to a divergent-convergent nozzle, the outer tube in fluid communication with the propellant gas stream;  
an ionizer for ionizing the propellant gas, the ionizer located between the gas propellant source and the outer tube;  
a source for a heated, pressurized gas stream;  
a source for ozonated, deionized water;  
a mixer for mixing deionized water from the deionized water source with the gas stream from the gas source and forming a gas-liquid mixture;  
a capillary steam generation system for receiving the gas-liquid water mixture and forming a gas-water vapor mixture from the gas-liquid water mixture.

18. The system in accordance with claim 12 wherein the coaxial delivery line is constructed of stainless steel, Teflon, polyetheretherketone or combinations thereof.



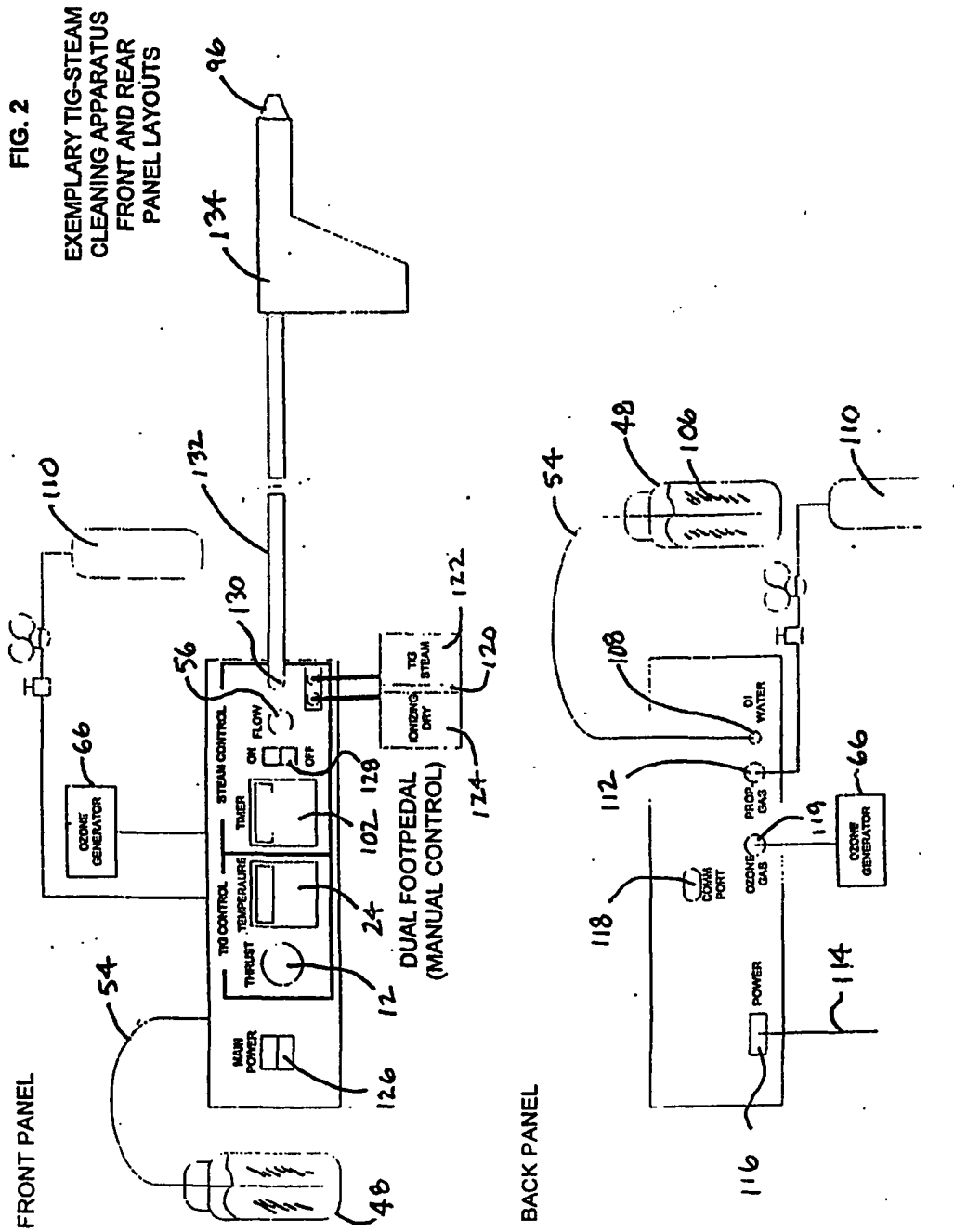


FIG. 3

EXEMPLARY TIG-STEAM  
SPRAY NOZZLE

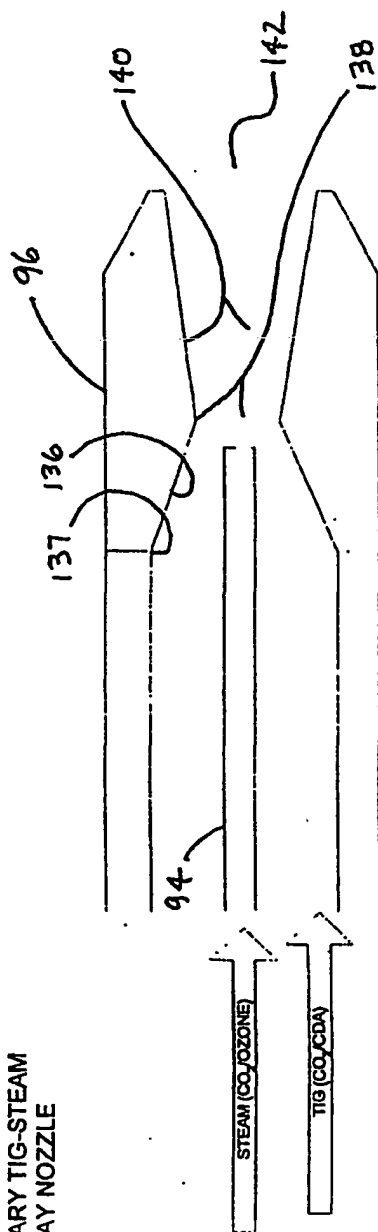
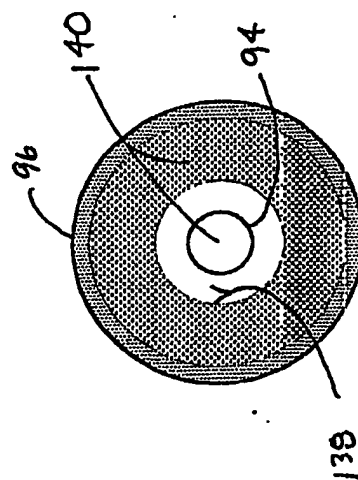


FIG. 4

EXEMPLARY TIG-STEAM  
SPRAY NOZZLE  
(END VIEW)



FIGS. 5a,b,c  
EXEMPLARY TIG-STEAM  
CLEANING PROCESS

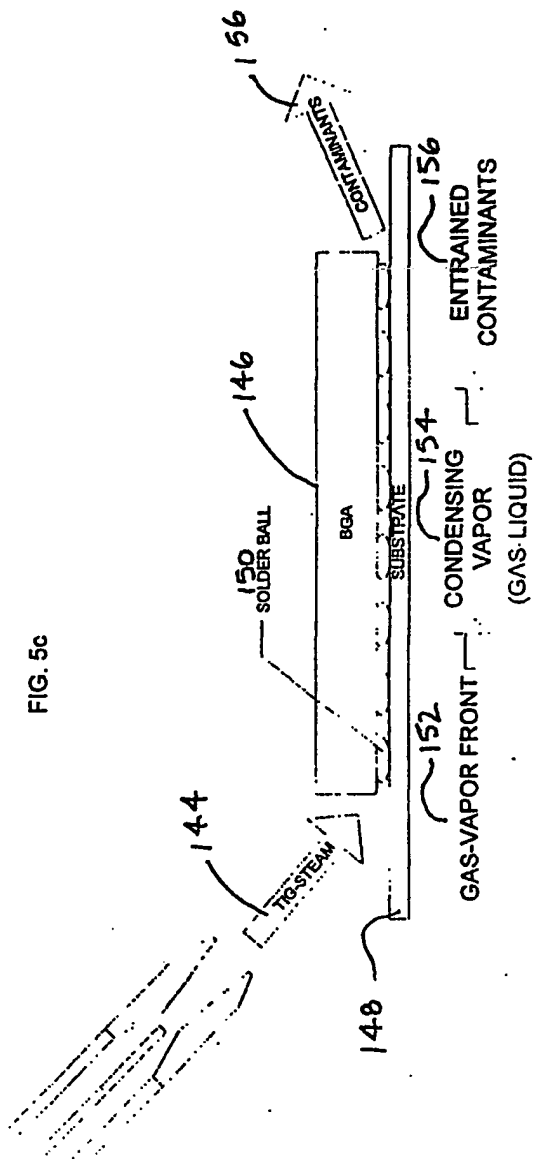
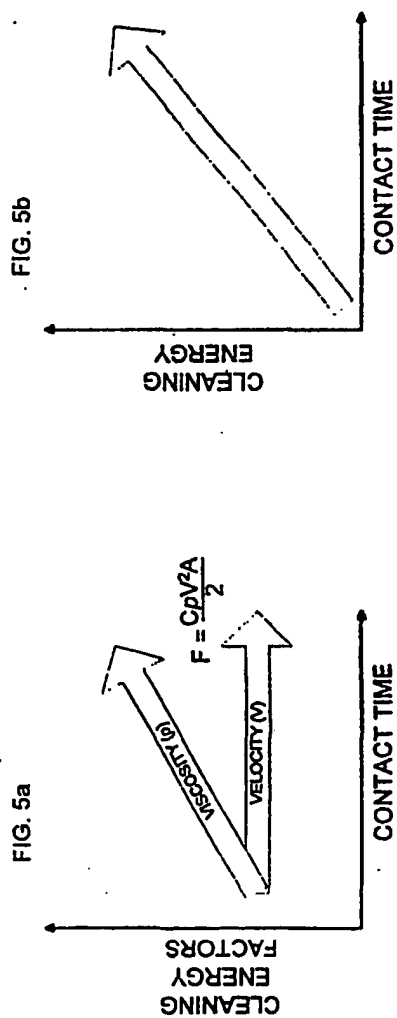




FIG. 6  
EXEMPLARY TIG-STEAM  
CLEANING PROCESS

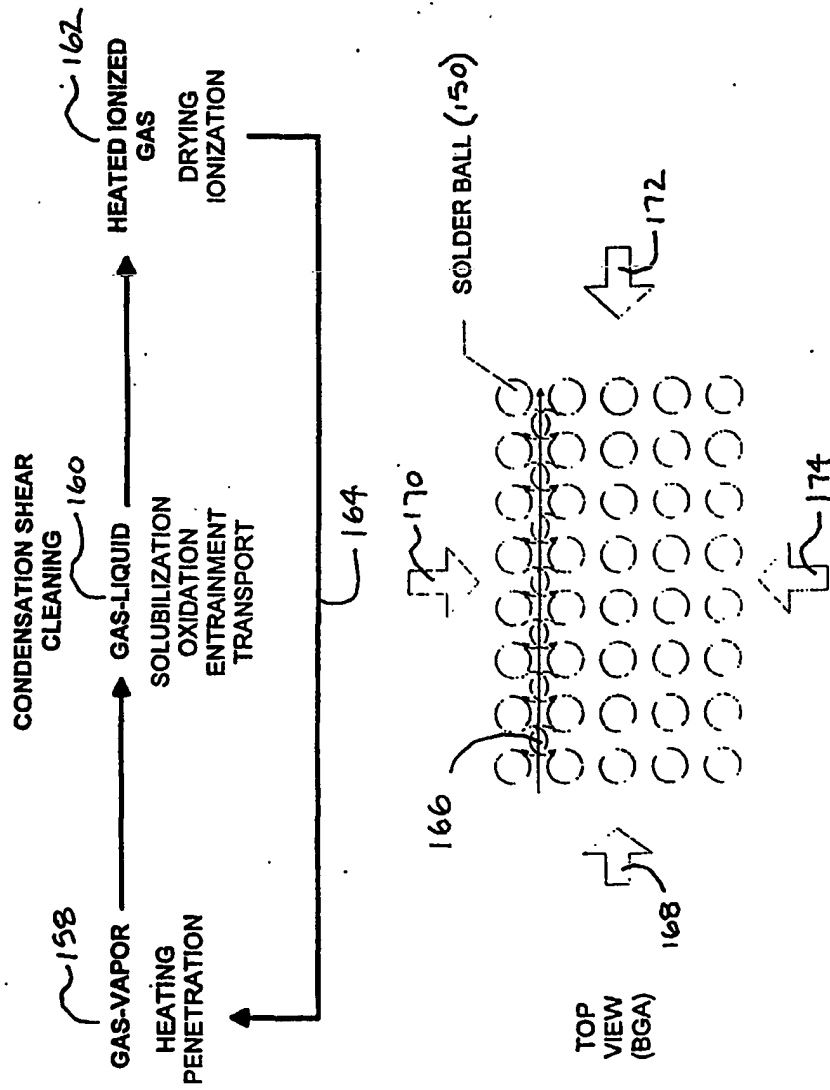
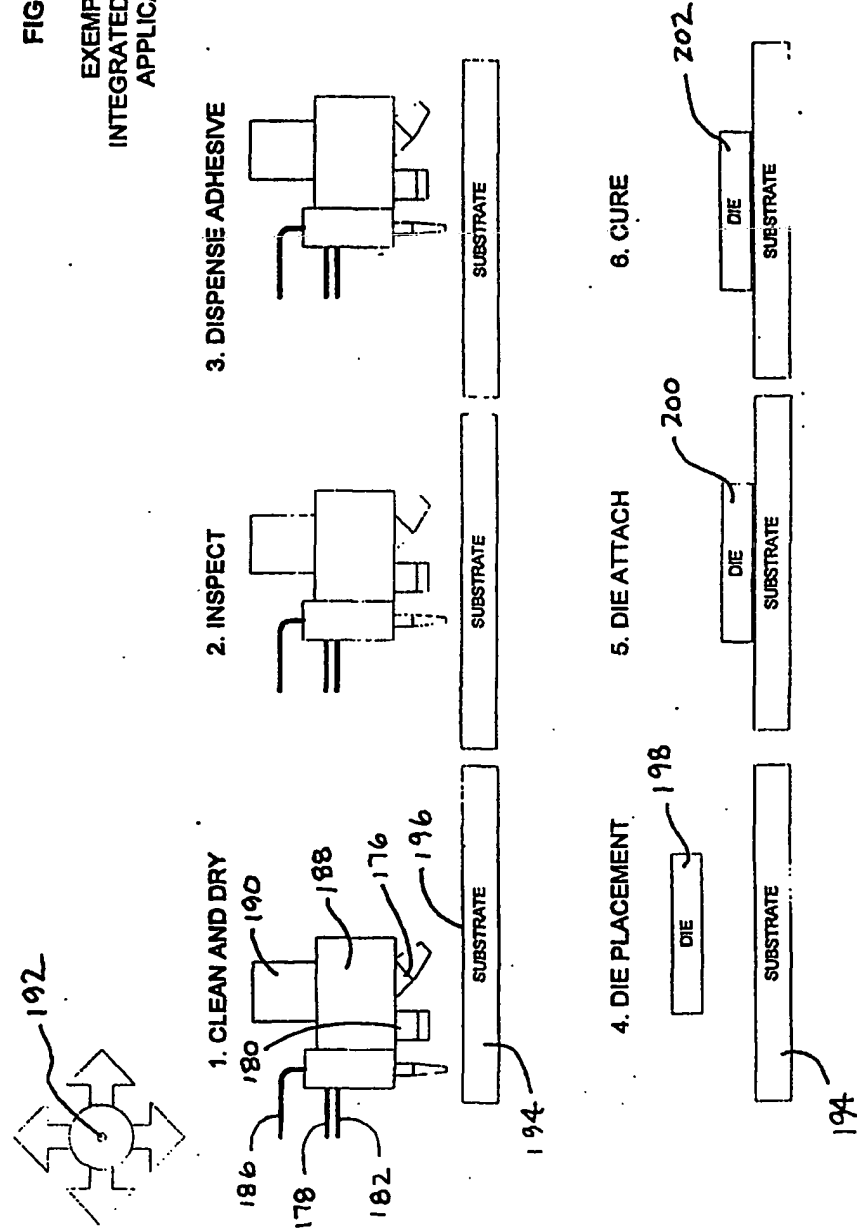


FIG. 7  
EXEMPLARY  
INTEGRATED CLEANING  
APPLICATION



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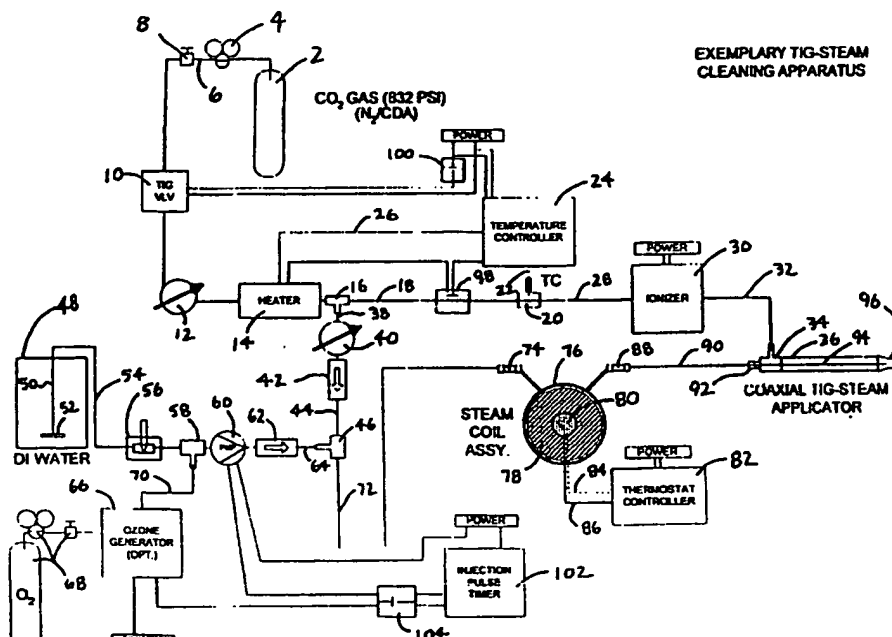
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[Continued on next page]

(54) Title: GAS-VAPOR CLEANING METHOD AND SYSTEM THEREFOR



(57) Abstract: Disclosed is a method and apparatus for cleaning using a gas-vapor mixture. A heated, pressurized stream of propellant gas is supplied to the outer tube (36) of a coaxial delivery line (132). The coaxial delivery line (132) is formed of an outer tube (36) and an inner tube (94) operably connected to a divergent-convergent mixing nozzle (96). A stream of a pre-heated gas is mixed with deionized water to form a gas-liquid mixture, which is heated to form a gas-vapor mixture. The gas-vapor mixture is then fed to the inner tube (94) of the coaxial delivery line (132). The gas-vapor mixture spray exiting the mixing nozzle (96) is then directed at an article to be cleaned.



— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

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## A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 730 806 A (CAIMI ET AL) 24 March 1998 (1998-03-24) cited in the application abstract column 2, line 40 -column 3, line 51; figures	1,4, 9-13,17
A	WO 99 34422 A (APPLIED MATERIALS, INC.) 8 July 1999 (1999-07-08) abstract page 2, line 10 - line 30 page 4, line 22 -page 6, line 6; figures	1,10,13, 17
A	US 3 788 825 A (ARENSON) 29 January 1974 (1974-01-29) abstract column 3, line 18 -column 5, line 44; figures	1,10,13, 17
	-/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 725 154 A (JACKSON) 10 March 1998 (1998-03-10) cited in the application abstract column 2, line 10 - line 16 column 3, line 62 -column 4, line 7 column 4, line 53 - line 67; figures	1,2,6, 10,13, 14,17
A	FR 2 145 864 A (V. N.-I. INSTITUT ELEKTROTERMICHESKOGO OBOURODOVANIA VNIIE TO) 23 February 1973 (1973-02-23) page 2, line 16 -page 3, line 25; figures	1,10,13, 17
A	US 4 615 352 A (GIBOT) 7 October 1986 (1986-10-07) abstract column 2, line 10 -column 3, line 12; figures	1,2,10, 13,17
A	DATABASE WPI Section Ch, Week 199015 Derwent Publications Ltd., London, GB; Class J02, AN 1990-114446 '25! XP002194649 -& SU 1 489 812 A (SHTRAL ET AL), 30 June 1989 (1989-06-30) abstract	1,10,13, 17
A	US 5 372 754 A (ONO) 13 December 1994 (1994-12-13) abstract column 2, line 52 -column 3, line 13 column 4, line 64 -column 5, line 8; figures	1,10,13, 17

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/24341

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5730806	A	24-03-1998	NONE	
WO 9934422	A	08-07-1999	US 6332470 B1 TW 436916 B WO 9934422 A1	25-12-2001 28-05-2001 08-07-1999
US 3788825	A	29-01-1974	NONE	
US 5725154	A	10-03-1998	NONE	
FR 2145864	A	23-02-1973	FR 2145864 A5	23-02-1973
US 4615352	A	07-10-1986	FR 2564566 A1 AU 571408 B2 AU 4222885 A CA 1280068 A1 DE 3517513 A1 ES 543194 D0 ES 8608134 A1 IT 1200474 B ZA 8503441 A	22-11-1985 14-04-1988 21-11-1985 12-02-1991 21-11-1985 01-06-1986 16-11-1986 18-01-1989 24-12-1985
SU 1489812	A	30-06-1989	SU 1489812 A1	30-06-1989
US 5372754	A	13-12-1994	JP 6291040 A	18-10-1994